THE CRYSTAL STRUCTURE OF GLYCOCYAMINE HYDROBROMIDE

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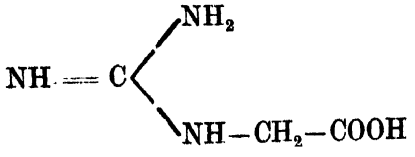
ABSTRACT. Crystals of glycocyamine hydrobromide, $C_3H_7O_2N_3$. HBr, belong to the monoclinic space group $P2_1/c$ with cell dimensions a = 5.53Å, b = 13.52Å, c = 9.20Å and $\beta = 92°$. There are four molecules per unit cell. The structure has been solved by three dimensional Patterson and heavy atom (bromine) phased Fourier syntheses. The coordinates of the atoms (hydrogen atoms excluded) with their isotropic temperature factors have been refined by two-dimensional least-squares method. The molecule of glycocyamine is characterised by two planar groups, e.g. the carboxyl group and the guanidyl group. The molecule is not a zwitterion, the two C—O bond lengths in the carboxyl group being 1.28 Å and 1.34 Å. The molecules in the crystal are held together by a three-dimensional network of hydrogen bonds of the types N—H——O, N—H——Br and O—H——Br.

INTRODUCTION

Glycocyamine or guanidoacetic acid has the following chemical formula :



Though not included in the list of standard amino acids, guanidoacetic acid, like amino acetic acid (glycine), plays an important biological role so far as the formation of creatine, a metabolic product of great interest, in the living system is concerned. Glycocyamine forms a part of our general program of study of the influence of various substited groups in the α-amino or the side chain groups of different amino acids on their crystal structure, configuration and electronic charge distribution. The study of the structure of glycocyamine in the form of its different hydrohalides and metal complexes is in progress in our laboratory. This short communication deals with the crystal structure of glycocyamine hydrobromide.

UNIT CELL AND SPACE GROUP

Single crystals of glycocyamine hydrobromide were grown in the form of colourless plates by slow evaporation of an aqueous solution of this compound

at room temperature. Due to long exposure to ordinary atmospheric conditions, the sample was found to lose its single crystal characteristics. The crystal was, therefore, coated with durofix and kept in a sealed thin walled glass capillary for taking X-ray photographs. The unit cell dimensions as determined from rotation and Weissenberg photographs are :

$$a = 5.53\text{Å}, \quad b = 13.52\text{Å}, \quad c = 9.20\text{Å}, \quad \beta = 92°.$$

The systematic absences of *hol* reflections with l odd and oko with k odd indicate that the space group is $P2_{1/c}$. The density of the crystal as determined by the method of floatation is 1.85g cm^{-3}, while the calculated value assuming four formula units of $C_3H_7O_2N_3.HBr$ is 1.89g.cm^{-3}

Three dimensional intensity data were collected about a and c axes by multiple film equi-inclination Weissenberg technique using CuKα radiation. The intensities were estimated visually and corrected for spot size, Leorentz and polarisation factors. The linear absorption co-efficient of the crystal for CuKα radiation was 82 cm^{-1}. No correction for absorption was, however, made at the initial stage but due to slow convergence of refinement it was found necessary to make the absorption correstion at a later stage of refinement. The intensity data obtained from different layers were put on the same relative scale by cross layer correlation method and were put on the absolute scale by Wilson's method.

STRUCTURE DETERMINATION

The positions of the four heavy atoms (Bromine) in the unit cell were determined from two Patterson projections on (100) and (001) shown in Fig. 1 and Fig. 2. An attempt to derive the structure from these two sets of intensity data, i.e. *okl* and *hko* reflections, was not successful. Consequently, three dimensional intensity data were used for the determination of the structure. A three dimensional Fourier synthesis was calculated using observed structure amplitudes to which phases were assigned from four bromine atoms. The computation for Fourier summation was done on the C.D.C. 3600 computer using Fourier program written and kindly supplied to us by Dr. Blount. The Fourier synthesis revealed the structure completely. Structure factors for all reflections were then calculated using the co-ordinates of all the atoms in the molecule and the disagreement factor $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ was found to be 32%.

The atomic parameters have been refined by the least squares method on IBM 1620 using G. A. Mair's program. The R value at this stage came down to 16.6% and 18.6% for *okl* and *hko* reflections respectively. The atomic parameters at this stage of 2D-refinement are given in table I. Intramolecular and

intermolecular bond lengths and angles are given in table II and III and digrammatically shown in fig. 3 and fig. 4 respectively.

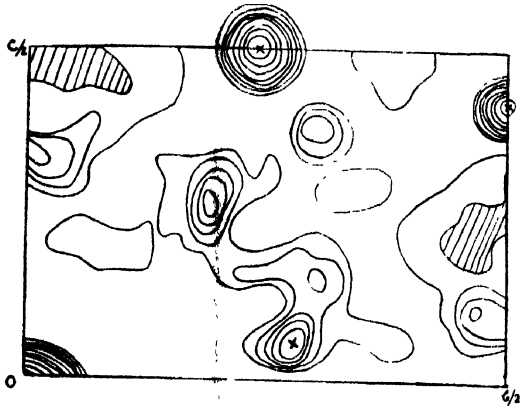


Fig. 1. Patterson synthesis of glycocyamine hydrobromide projected on (100). The Br—Br peaks are indicated by crosses.

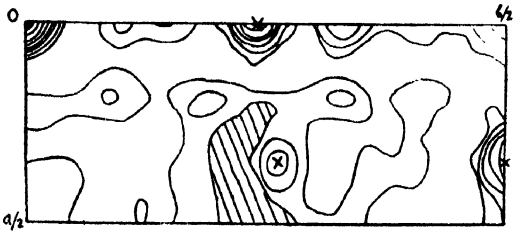


Fig. 2. Patterson synthesis of glycocyamine hydrobromide projected on (001). The Br—Br peaks are indicated by crosses.

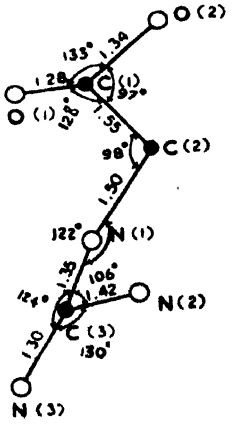


Fig. 3. Bond lengths and bond angles of glycocyamine hydrobromide.

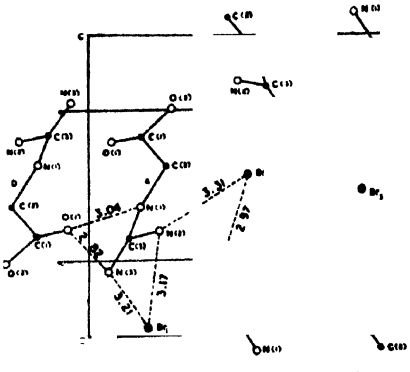


Fig. 4. Projection of the structure along the *a* axis. The dashed lines indicated the hydrogen bonds.

DISCUSSION OF THE STRUCTURE

The two C-O bond distances in the carboxyl group of glycocyamine hydrobromide have been found to be C(1)—O(1) = 1.28Å and C(1)—O(2) = 1.34Å. This indicates that the hydrogen atom is bound to the carboxyl oxygen O(2). The bond distances C(2)—C(1) = 1.55Å and C(2)—N(1) = 1.50Å (table I and fig. 3) agree well with the average values 1.35Å and 1.50Å respectively for these bonds, as deduced by Hahn (1957) from other amino acids. The three C—N bond distances in the guanidly group of glycocyamine hydrobromide i.e. C(3)—N(3) = 1.30Å, C(3)—N(2) = 1.42Å and C(3)—N(1) = 1 35Å compare well with those of Arginine hydrobromide (Wyckoff, 1966) but are slightly different from those of arginine dihydrate (Karle *et al*, 1964).

TABLE I

Glycocyamine hydrobromide : Atomic co-ordinates and temperature factor

Atom	*x/a*	*/b*	*z/c*	*B*(Å)
Br.	.1695	.1340	.0301	1.71
N(1)	.7265	.1249	.4397	3.00
N(2)	.3649	.1687	.3528	1.00
N(3)	.5986	.0404	.2295	1.00
C(1)	.8363	.1235	.6802	2.74
C(2)	.6610	.1790	.5737	4.00
C(3)	.5619	.1033	.3332	0.81
O(1)	.9889	.0560	.6508	2.18
O(2)	.8134	.1840	.7938	3.11

TABLE II

Glycocyamine hydrobromide : Intramolecular bond lengths and bond angles

Bond length	Å	Bond angle	
C(1)—O(1)	1.28	O(1)—C(1)—O(2)	133°
C(1)—O(2)	1.34	O(1)—C(1)—C(2)	128°
C(1)—C(2)	1.55	O(2)—C(1)—C(2)	97°
C(2)—N(1)	1.50	C(1)—C(2)—N(1)	98°
N(1)—C(3)	1.35	C(2)—N(1)—C(3)	122°
C(3)—N(2)	1.42	N(1)—C(3)—N(2)	106°
C(3)—N(3)	1.30	N(1)—C(3)—N(3)	124°
		N(3)—C(3)—N(2)	130°

TABLE III

Intermolecular bond distances and angles

Hydrogen bond lengths	Å	Hydrogen bond angles	
N(1)—H ....O(1)	3.04	C(1)—O(2) ....Br	111°
N(3)—H ....Br	3.21	C(2)—N(1) ....O(1)	140°
N(2)—H ....Br	3.17	C(3)—N(1) ....O(1)	88°
N(2)—H ....Br	3.31	C(3)—N(3) ....O(1)	85°
N(3)—H ....O(1)	2.82	C(3)—N(C) ....Br	92°
O(2)—H ....Br	2.97	C(3)—N(2) ....Br	146°
		C(3)—N(2) .. .Br	91°

The molecular packing of glycocyamine hydrobromide molecules in the crystal viewed along a axis is shown in Figb.4. There are six hydrogen atoms in each molecule of glycocyamine hydrobromide available for hydrogen bond formation, one from the carboxyl group—COOH and five from the guanidyl ion $NH_2-C(NH_2)-NH-$. The guanidyl ion makes three hydrogen bonds with bromine ions and two with carboxyl oxygens. The hydrogen atom attached to the carboxyl oxygen O(2) makes hydrogen bond with bromine ion. Thus all the hydrogen atoms available for hydrogen bond formation or in the other words all the available sites for hydrogen bond formation have been satisfactorily accounted for.

Further structural details and conformation will be published elsewhere in due course.

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